STANDARD OPERATING PROCEDURE

Bromide Analysis In Soil by Ion Selective Electrode

KEY WORDS

Electrode, ISE, ISA

APPROVALS

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1.0 INTRODUCTION

The Environmental Monitoring Branch uses bromide solutions as conservative tracers for the movement of water in the soil.

1.1 Purpose

This standard operating procedure provides instructions for determining bromide concentration in soil samples using an Orion® ion selective electrode method (ISE). When utilizing an alternative brand of electrode, it may be necessary to modify these standard operating procedures.

2.0 MATERIALS

2.1 100 mL volumetric flasks-1 per standard

2.2 125 mL Erlenmeyer flasks-1 per sample

2.3 50 mL beakers-1 per sample

2.4 2 L volumetric flask

2.5 Orion® single junction reference electrode #900100

2.6 Orion® bromide selective electrode #943500

2.7 Corning® model 250 pH meter or equivalent

2.8 Filter funnels and stand

2.9 2 50-mL burettes and burette stand

2.10 Balance with resolution to 0.00 g

2.11 Magnetic stirrer

2.12 Orbital Shaker

2.13 12.5 cm #42 Whatman® filter papers

2.14 Parafilm®

2.15 10 mL volumetric pipette

2.16 25 mL volumetric pipette

2.17 1-10 mL Rainin® pipette or equivalent

2.18 Orion® reference electrode filling solution #90-00-01 (saturated with AgCl)

2.19 Orion® bromide standard solution #943506 (0.1 M NaBr=7990 ppm) or equivalent

2.20 Orion® ionic strength adjustor solution #940011 (5 M $NaNO_3$) or equivalent

2.21 Deionized (DI) or distilled water

3.0 PROCEDURES

Stock solutions should be prepared once a week.

3.1 Instructions for Preparing Stock Solutions

3.1.1 Prepare a 100-ppm bromide stock solution by measuring 25 mL of 0.1M NaBr (7990 ppm) into a 2 L volumetric flask using a 25 mL volumetric pipette. Add deionized (DI) (or distilled) water to bring the volume up to 2 L.

3.1.2 Prepare a 10-ppm bromide stock solution by measuring 25 mL of 100-ppm bromide stock solution into a 250 mL volumetric flask using a 25 mL volumetric pipette. Add DI water to bring the volume up to 250 mL.

3.1.3 Record the date on all flasks.

3.2 Instructions for Preparing Standards

The bromide standards must narrowly bracket the range of the expected bromide concentration in the soil samples. The concentration of at least two standards must be an order of magnitude apart and in the linear measurement range of the electrode (≥0.5 ppm). Prepare the following standards daily at the concentrations required to narrowly bracket the sample range (The additional volume of the 5 ppm standard will be required for spiking soil samples for quality control purposes).

3.2.1 Preparation of a 50 ppm bromide standard: Using a volumetric pipette, add 125 mL of the 100 ppm bromide stock solution to a 250 mL volumetric flask. Add 5 mL of 5M ionic strength adjustor (ISA) to the flask. (Bromide ISE's are typically sensitive to matrix effects. Adding an ISA to the standards and samples in order to standardize the ionic strength between the solutions can minimalize these effects). Bring the volume up to 250 mL with DI water.

3.2.2 Preparation of a 10-ppm bromide standard: Using a 25 mL volumetric pipette, add 25 mL of the 100 ppm bromide stock solution to a 250 mL volumetric flask. Add 5 mL of 5M ISA to the flask. Bring the volume up to 250 mL with DI water.

3.2.3 Preparation of a 5-ppm bromide standard: Using a 25 mL volumetric pipette, add 25 mL of the 100 ppm bromide stock solution to a 500 mL volumetric flask. Add 10 mL of 5M ISA to the flask and then add DI water to bring the volume up to 500 mL.

3.2.4 Preparation of a 1-ppm bromide standard: Using a 1-10 mL Rainin® pipette or equivalent, add 2.5 mL of the 100 ppm bromide stock solution to a 250 mL volumetric flask. Add 5 mL of 5M ISA to the flask. Bring the volume up to 250 mL with DI water.

3.2.5 Preparation of a 0.1-ppm bromide standard: Using a 1-10 mL Rainin® pipette or equivalent, add 2.5 mL of the 10 ppm bromide stock solution to a 250 mL volumetric flask. Add 5 mL of 5M ISA to the flask. Bring the volume up to 250 mL with DI water.

3.2.6 Preparation of a 0.2-ppm bromide standard: Using a 1-10 mL Rainin® pipette or equivalent, add 5 mL of the 10 ppm bromide stock solution to a 250 mL volumetric flask. Add 5 mL of 5M ISA to the flask. Bring the volume up to 250 mL with DI water.

3.2.7 Preparation of a 0.3-ppm bromide standard: Using a 1-10 mL Rainin® pipette or equivalent, add 7.5 mL of the 10 ppm bromide stock solution to a 250 mL volumetric flask. Add 5 mL of 5M ISA to the flask. Bring the volume up to 250 mL with DI water.

3.2.8 Preparation of a 0.4-ppm bromide standard: Using a 1-10 mL Rainin® pipette or equivalent, add 10 mL of the 10 ppm bromide stock solution to a 250 mL volumetric flask. Add 5 mL of 5M ISA to the flask. Bring the volume up to 250 mL with DI water.

3.2.9 Preparation of a 0.5-ppm bromide standard: Using a 1-10 mL Rainin® pipette or equivalent, add 12.5 mL of the 10 ppm bromide stock solution to a 250 mL volumetric flask. Add 5 mL of 5M ISA to the flask. Bring the volume up to 250 mL with DI water.

3.2.2 Record the date on all flasks.

3.3 Instructions for Preparing Samples

3.3.1 Place soil samples in labeled jars and oven-dry at 105° C for 24 hours or until weights become constant. Grind soil with mortar and pestle to break apart soil aggregates. For each sample weigh out 50.00 g of oven-dried soil into a labeled 125 mL Erlenmeyer flask. Record the sample number and flask number on a data sheet for each sample. Prepare two additional soil samples to be used for the duplicate and matrix-spiked samples for quality control purposes (see QC section for spiking procedure).

3.3.2 Add 50 mL of 0.1M ISA to each flask containing a soil sample, dispensing the ISA from a burette. (To make 0.1M ISA, add 40 mL of 5M $NaNO_3$ to a 2 L flask. Bring the volume up to 2 L with DI water).

3.3.3 Cover the top of each flask with parafilm and place the flask on an orbital shaker for 30 minutes at a speed of approximately 220 RPM.

3.3.4 Using the filter funnels filter each sample through #42 Whatman® filter paper into labeled 50 mL beakers.

3.4 Check Slope of the Bromide Response Curve on the Meter

3.4.1 Ensure that the expected bromide concentration in the soil samples is within the measurement range of the bromide electrode. Follow the manufacturer's instructions for preparing the reference electrode. Attach the bromide electrode, single junction reference electrode, temperature sensor, and ion stirrer to the pH meter.

3.4.2 Press the 'mode' button on the pH meter until the unit displayed is 'mV.'

3.4.3 Place electrodes, magnetic stir bar, and temperature sensor in either the 50-, 10-, or 5-ppm bromide standard, based on the expected bromide concentration of the soil sample. Turn on stirrer and mix standard for 30 seconds. When meter indicates that the reading is stable, record the millivolt (mV) reading on the calibration sheet. Lift sensors from the standard, rinse with DI water and blot with a kimwipe.

3.4.4 Repeat step 3.4.3 with the remaining bromide standard(s) in the linear range (≥0.5 ppm). Record the mV reading(s) on the

calibration sheet. Ensure that the difference in the mV readings between two standards with bromide concentrations an order of magnitude apart is 57 ± 2 mV. (For example, the difference in readings between the 50- and 5-ppm bromide standards should be 57 ± 2 mV). If the difference is out of range, repeat steps 3.4.3 and 3.4.4. If difference is still out of range, prepare new standards and repeat.

3.4.5 Take mV readings in the nonlinear range using the 0.4-, 0.3-, 0.2-, and 0.1-ppm bromide standards. Record the results.

3.4.6 Take a mV reading of the 0.1M ISA used to prepare samples. This will be the reading for the blank. Record the result.

3.5 Instructions for Reading Samples

Repeat step 3.4.3 above using your samples instead of standards. Ensure calibration checks are conducted periodically as indicated in section 4.2. Record the readings on the sample data sheet.

3.6 Instructions for Recording Data

Record all calibration data. Include the date and temperature. Make sure the temperature doesn't vary more than one degree Celsius from the time of calibration until the last sample is read.

4.0 QUALITY CONTROL FOR BROMIDE ANALYSIS

4.1 Duplicate Sample

Prepare a duplicate sample using additional soil from one sample associated with the set of samples being analyzed for bromide concentration. Measure the mV reading and record the result. A 15% relative difference in bromide concentration between the sample and its duplicate will be acceptable.

4.2 Calibration Check

Measure the 0.5-ppm standard after every 5th sample and compare the result to the initial 0.5-ppm reading. The recovery of bromide should be

within 10% of the initial recovery (USEPA test methods guidance for bromide analysis by ISE). At 0.5-ppm bromide concentration, a 10% bromide recovery equates to about ±3 mV of the original mV reading. If the subsequent reading is beyond the ±3 mV range of the initial reading, then the instrument needs to be recalibrated. All samples analyzed since the last acceptable calibration check must be re-analyzed.

4.2 Matrix Spike Sample

Prepare one matrix spike sample daily as follows: Place 50 g of dried soil that contains either no bromide or a known concentration of bromide into a 50 mL flask. Add 50 mL of 5-ppm bromide standard (which already contains ISA) to the flask. Shake and filter the sample as specified in section 3.3.3 and 3.3.4. Following the procedure outlined in 3.4.4, record the mV reading of the matrix spike sample. Bromide recovery from the spike sample must be within 25% of 5 ppm (USEPA test methods guidance for bromide analysis by ISE), or within 25% of the sum of 5.0 ppm and the original concentration of bromide in the soil sample. If the recovered bromide concentration is not within 25% of the expected amount, then the instrument needs to be recalibrated. All samples analyzed in the sample set also need to be re-analyzed.

5.0 CALCULATIONS

5.1 Prepare a calibration curve using the readings from the standards by plotting mV as a function of the logarithm of bromide concentration. Using a spreadsheet or statistical software, determine the slope (b) and intercept (a) for the function y=a+bx, where mV is the independent variable (x) and the log of bromide concentration is the dependent variable (y). The function only holds for bromide concentrations of 0.5 ppm and higher (the linear range for mV as a function of the logarithm of bromide concentration). Estimate the bromide concentration of the samples by determining the antilog of the function after solving for each sample's mV reading.

5.2 A non-linear calibration curve needs to be prepared from the 0.1-, 0.2-, 0.3-, and 0.4- ppm bromide standards using a curve-fitting software program. The mV reading is plotted as a function of the logarithm of bromide concentration. Samples with mV readings above that of the 0.5 ppm standard are in the non-linear range. Estimate bromide concentrations of these samples by determining the antilog of the non-linear function after solving the function for each sample's mV reading.

5.3 Estimated concentration of bromide on a dry soil basis is numerically equivalent to the concentration measured in the aqueous solution:

$$ppm\ \text{bromide} = \frac{mg\ \text{bromide}}{L\ \text{solution}} \text{ x } \frac{1000mL\ \text{solution}}{1000g\ \text{dry soil}} = \frac{mg\ \text{bromide}}{kg\ \text{dry soil}}$$

Estimation of total bromide residues in a segmented soil core requires the bulk density value (SOP FSSO001.00) for each soil segment. Total bromide mass is calculated by summing the bromide mass of each soil segment on an area basis:

$$\frac{mg\ \text{bromide}}{kg\ \text{dry soil}} \text{ x } \frac{kg\ \text{dry soil}}{dm^3\ \text{soil}} \text{ x } \frac{1000dm^3\ \text{soil}}{m^3\ \text{soil}} \text{ x } \frac{m\ \text{soil segment length}}{1} = \frac{mg\ \text{bromide}}{m^2\ \text{soil}}$$

6.0 ELECTRODE MAINTENANCE AND STORAGE

As the membranes of the Orion® electrode are very susceptible to contamination or drying out, it is important that they are maintained and stored properly.

6.1 Storage of the Orion® Bromide Selective Electrode #943500

The Orion® bromide selective electrode #943500 should be rinsed thoroughly with distilled water after use, and stored in the open air. For long-term storage, replace the electrode cap and store dry.

6.2 Storage of the Orion® Single Junction Reference Electrode #900100

The Orion® single junction reference electrode #900100 may be stored in the open air in between uses for as long as two hours. For storage periods of up to one week, the electrode should be stored in filling solution or distilled water. Do not allow the solutions inside the electrode to dry up, causing crystallization. For storage periods longer than one week, drain both chambers in the electrode of the filling solution, flush the inside with distilled water, and store dry.

6.3 Electrode Maintenance

To clean both the Orion® bromide electrode and the Orion® reference electrode, place a drop of liquid dish detergent on a moist cloth and gently rub it on the sensing element. Rinse with distilled water. If the electrode measurements become sluggish or erratic, and the above cleaning

method does not improve its performance, try polishing the electrode using the following method. Detach a 1-inch long piece of Orion® 948201 polishing strip. Hold the electrode with the sensing element facing upwards, and put a few drops of distilled water on the sensing element surface. With the frosted side down, place the polishing strip on the sensing element surface and hold in place gently with your finger. Rotate the electrode for about 30 seconds, and then rinse and soak the electrode in a 1-ppm (or 10^{-5} M Br^-) standard solution for about two minutes. The electrode will now be ready for use.

7.0 SAFETY

When handling bromide, wear protective gloves and clean body-covering clothing. Use chemical safety goggles. Maintain eye wash fountain and quick-drench facilities in work area. Precautions should be taken to prevent potential ingestion of particles containing bromide. Refer to the bromide Material Safety Data Sheet for ventilation and respirator requirements, and for other safety related information. http://www.sciencelab.com/xMSDS-Potassium_bromide-9927400

8.0 REFERENCES

USEPA test methods guidance for bromide analysis by ISE. <http://www.epa.gov/sw-846/pdfs/9211.pdf>